

3 HIGH ORDER COLLISION INTEGRALS 4

by

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4 Final report on the completed contract (NSR 52-112-001) for the
National Aeronautics and Space Administration on the calculation of
higher order collision integrals.

Abstract:

High order collision integrals have been calculated for the
potentials $V(r) = Ae^{-r/p}$ and $\pm C/r^n$ for $n = 2, 3, 4, 5, 6, 8, 10,$
15, 25, 50. These should enable transport properties to be calculated
for these potentials to a higher accuracy than previously. Some
previous calculations of collision integrals for these potentials
have been checked.

N 67-33024

FACILITY FORM 602	(ACCESSION NUMBER)	(THRU)
	10/RS22-25	
	(PAGES)	(CODE)
	CR-8699/1 N1	24
	(NASA CR OR TMX OR AD NUMBER)	(CATEGORY)

1. Introduction

The interaction potential between atoms and molecules at short internuclear distances, r , can be approximated over a wide range of r by either the exponential repulsive potential $V(r) = Ae^{-r/\rho}$ or by the inverse power potential $\pm C/r^n$. Some transport collision integrals for the first of these potentials have been computed by Monchick (1959) and for the second ($n = 2, 3, 4, 6, 8, 10, 12, 14, \infty$) by Kihara, Taylor and Hirschfelder (1960). All of the high order collision integrals needed to compute accurately the high order approximations to the transport coefficients were not calculated in either case. In this paper we check these earlier calculations and compute the collision integrals not previously calculated. We also compute the collision integrals for some additional high values of n in the case of the inverse power potentials.

2. Exponential Repulsive Potential

We adopt the usual definition of the collision integral $\Omega^{(l,s)}$ given by Hirschfelder, Curtiss and Bird (1964). We follow Monchick (1959) and define a temperature parameter

$$\alpha = \ln(A/kT) \quad (1)$$

for the potential

$$V(r) = A e^{-r/\rho} \quad (2)$$

where k is Boltzmann's constant and T is the absolute temperature.

We also define the dimensionless collision integrals $I_{(\ell,s)}$ by

$$\Omega^{(\ell,s)} = (8\pi kT)^{\frac{1}{2}} \alpha^2 \rho^2 I_{(\ell,s)}. \quad (3)$$

The collision integrals $I_{(1,s)}$ ($s = 1$ to 5); $I_{(2,s)}$ ($s = 2$ to 4); $I_{(3,3)}$ have been calculated by Monchick for a range of α between 3.50 and 28.50. To compute the high order approximations to the transport coefficients the collision integrals $I_{(2,5)}$; $I_{(2,6)}$; $I_{(3,4)}$; $I_{(3,5)}$; $I_{(4,4)}$ are needed.

The collision integrals were computed by the method described in detail by Smith and Munn (1964). Indeed the original programme by Smith and Munn built for an IBM 7090 computer was adopted for the ICT 1905 computer owned by Queen's University. Details are given in a thesis by Higgins (1967). Because the range of the parameter was large an initial run gave some poor results. This was corrected by breaking the production run into two parts: one from $\alpha = 3.5$ to 13.0, the second from $\alpha = 13.5$ to 28.5.

The collision integrals $I_{(1,1)}$; etc. thus calculated were in agreement with those of Monchick to better than one part in 1,000 in all cases where comparisons with Monchick were possible. We are therefore confident that the remaining 5 sets of collision integrals shown in Table 1 are correct to the same accuracy and that Monchick's results are correct at least to this accuracy.

3. Inverse Power Potentials

Kihara et al. have shown that the collision for the potential:

$$V(r) = \pm c/r^n \quad (4)$$

can be expressed in the form

$$\Omega^{(l,s)} = \left(\frac{n k T}{2\mu}\right)^{\frac{1}{2}} \left(\frac{nc}{kT}\right)^{\frac{2}{n}} T(s+2-\frac{2}{n}) A^l(n) \chi(s)$$

where

$$A^l(n) = \frac{1}{2} \int_0^\pi (1 - \cos^l \chi) d\beta^2 \quad (6)$$

and

$$\beta = b(E/nc)^{1/n} \quad (7)$$

In these formulas μ is the reduced mass, $\Gamma(x)$ is the Gamma function, x is the classical deflection function, b is the impact parameter and E is the energy of relative motion. In the programme already described the transport cross sections

$$Q^l(E) = 2\pi \int_0^{\infty} b(1 - \cos^l \chi) db \quad (8)$$

were calculated. From (6), (7) and (8) it is readily shown that

$$A^l(n) = \frac{1}{2\pi} \left(\frac{E}{nc} \right)^{\frac{2}{n}} Q^l(E) \quad (9)$$

and $A^l(n)$ is independent of the energy E .

The cross sections $Q^l(E)$ were computed for 4 energies in each case and $A^l(n)$ was computed from (9) in each case. The accuracy of the quantities $A^l(n)$ could be estimated from the agreement of the four values of $A^l(n)$.

The results for the repulsive potential are listed in Table 2 to the accuracy shown for $n = 2, 3, 4, 5, 6, 8, 10, 15, 25, 50$, and 100. Also shown are the results of Kihara et al. Agreement (in those cases where comparisons are possible) is excellent.

The results for the attractive - rigid potential (that is for the potential with an infinitesimal rigid core) are shown in Table 3. The comparison with the results of Kihara et al. is excellent

except in the case $n = 2$ when there is a difference of about 1 to 3 parts in 1,000. We are confident of the accuracy of our results to the number of figures quoted (except in this one case, the only case which gave us difficulty). The difficulty arises because if $n = 2$ and if $\beta < 1/\sqrt{2}$ the classical deflection angle equals $(-\infty)$. Therefore, between $\beta = 0$ and $1/\sqrt{2}$ we replaced it by a random phase, that is we replaced $\cos \chi$ by 0 if $l = 1$ or 3, by $\frac{1}{2}$ if $l = 2$ and by $\frac{1}{4}$ if $l = 4$. For β just above $1/\sqrt{2}$ the angle χ was very large and the integrand oscillated rapidly and was difficult to evaluate. Therefore, we believe that the Kihara et al. values should be used for $l = 1, 2$ and 3. In the case $l = 4$ our result should be correct to a few parts in 1,000. When the unreality of this physical model is realized it did not seem worthwhile computing this last number to a higher accuracy. The accuracy quoted should be sufficient.

4. Acknowledgments

I would like to thank Mr. L.D. Higgins who did almost all of the programming for the work in this contract. I would also like to thank the staff at the Computing Laboratory at The Queen's University for their services and especially Mr. Bernard Leeson for some late night computer runs.

Thanks are also due to the National Aeronautics and Space Administration for making this research possible.

References

- L. D. Higgins, Thesis, Queen's University of Belfast, N. Ireland, 1967.
- J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids (John Wiley & Sone, Inc., N.Y. 1954).
- T. Kihara, M. H. Taylor, and J. O. Hirschfelder, Phys. Fluids 3, 715, (1960).
- L. Monchick, Phys. Fluids, 2, 695, (1959).
- F. J. Smith and R. J. Munn, J. Chem Phys. 41, 3560, (1964).

Table 1 Collision integrals for the exponential repulsive potential

α	$I_{(2,5)}$	$I_{(2,6)}$	$I_{(3,4)}$	$I_{(3,5)}$	$I_{(4,4)}$
28.50	58.49	405.3	14.30	84.78	12.11
28.00	58.46	405.0	14.29	84.69	12.11
27.00	58.40	404.4	14.26	84.50	12.11
26.00	58.33	403.8	14.24	84.29	12.11
25.00	58.25	403.0	14.21	84.07	12.11
24.00	58.17	402.3	14.17	83.82	12.12
23.00	58.08	401.4	14.14	83.56	12.12
22.00	57.98	400.5	14.10	83.27	12.12
21.00	57.87	399.4	14.06	82.96	12.12
20.00	57.74	398.3	14.01	82.61	12.12
19.00	57.60	397.0	13.96	82.23	12.12
18.00	57.44	395.5	13.90	81.81	12.11
17.00	57.25	393.8	13.84	81.33	12.11
16.00	57.04	392.0	13.77	80.80	12.11
15.50	56.93	390.9	13.73	80.51	12.10
15.00	56.80	389.8	13.68	80.20	12.10
14.50	56.67	388.6	13.64	79.87	12.10
14.00	56.52	387.2	13.59	79.51	12.09
13.50	56.35	385.8	13.54	79.13	12.08
13.00	56.18	384.2	13.48	78.72	12.08
12.50	55.98	382.5	13.43	78.28	12.07
12.00	55.77	380.6	13.36	77.80	12.06
11.50	55.53	378.6	13.29	77.28	12.05
11.00	55.27	376.3	13.21	76.72	12.03
10.50	54.98	373.8	13.13	76.10	12.02

Collision integrals for the exponential repulsive potential (cont.)

α	$I_{(2,5)}$	$I_{(2,6)}$	$I_{(3,4)}$	$I_{(3,5)}$	$I_{(4,4)}$
10.00	54.66	371.0	13.04	75.43	12.00
9.50	54.29	367.9	12.94	74.69	11.98
9.00	53.88	364.3	12.83	73.86	11.95
8.75	53.65	362.4	12.76	73.42	11.93
8.50	53.41	360.3	12.70	72.95	11.92
8.25	53.15	358.1	12.63	72.45	11.90
8.00	52.87	355.7	12.56	71.93	11.88
7.75	52.57	353.2	12.48	71.37	11.86
7.50	52.24	350.4	12.40	70.78	11.83
7.25	51.89	347.5	12.32	70.14	11.80
7.00	51.51	344.3	12.22	69.47	11.77
6.75	51.10	340.8	12.13	68.75	11.74
6.50	50.65	337.1	12.02	67.98	11.70
6.25	50.16	333.0	11.91	67.15	11.66
6.00	49.62	328.6	11.78	66.26	11.61
5.75	49.03	323.7	11.65	65.30	11.56
5.50	48.38	318.3	11.51	64.26	11.50
5.25	47.66	312.4	11.35	63.14	11.43
5.00	46.86	305.9	11.18	61.91	11.35
4.75	45.97	298.6	11.00	60.58	11.26
4.50	44.97	290.5	10.79	59.11	11.15
4.25	43.84	281.5	10.57	57.50	11.04
4.00	42.57	271.3	10.32	55.73	10.90
3.75	41.12	259.7	10.05	53.76	10.74
3.50	39.47	246.7	9.74	51.58	10.55

Table 2 $A^{(l)}(n, \text{repulsive})$

n		$l = 1$	$l = 2$	$l = 3$	$l = 4$
2	Kihara et al.	0.3976	0.5278	0.7136	-
	Hirschfelder and Smith	0.3977	0.5281	0.7130	0.8137
3	Kihara et al.	0.3115	0.3533	0.472	-
	Smith	0.31126	0.3533	0.4722	0.5033
4	Kihara et al.	0.298	0.308	-	-
	Smith	0.29838	0.30847	0.41384	0.42226
5	Kihara et al.	-	-	-	-
	Smith	0.30007	0.29104	0.39325	0.38889
6	Kihara et al.	0.306	0.283	-	-
	Smith	0.30593	0.28317	0.38547	0.37226
8	Kihara et al.	0.321	0.279	-	-
	Smith	0.32022	0.27784	0.383275	0.35777
10	Kihara et al.	0.333	0.278	-	-
	Smith	0.33380	0.27748	0.38686	0.35279
15	Smith	0.36064	0.28140	0.39953	0.35160
25	Smith	0.39365	0.29011	0.41965	0.35720
50	Smith	0.43095	0.302806	0.44548	0.368404
100	Smith	0.45756	0.31334	0.46535	0.3787

Table 3 $A(l)$ (n, attractive - rigid)

n		$l = 1$	$l = 2$	$l = 3$	$l = 4$
2	Kihara et al.	0.8069	0.7110	1.1148	-
	Smith	0.809	0.708 ₅	1.112	1.007
3	Kihara et al.	0.6412	0.4641	-	-
	Smith	0.6411	0.463 ₅	0.771	0.636
4	Kihara et al.	0.5527	0.3852	0.6381	-
	Smith	0.5523	0.3846	0.6377	0.5122
5	Kihara et al.	-	-	-	-
	Smith	0.48207	0.34774	0.5540	0.4549
6	Kihara et al.	0.4342	0.3277	0.502	-
	Smith	0.4342 ₅	0.3276	0.49978	0.4235
8	Smith	0.38657	0.30613	0.44472	0.39038
10	Smith	0.370338	0.29669	0.422896	0.375244
15	Smith	0.369731	0.289038	0.410611	0.36103
25	Smith	0.392405	0.290850	0.420138	0.358649
50	Smith	0.4286727	0.3014206	0.4435732	0.3670490